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Ultrasonic Velocity Measurements in Water at Pressures to 10,000 kg/cm^2

by

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Ultrasonic-Velocity Measurements in Water at Pressures to 10,000 kg/cm^2

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ABSTRACT

Measurements of the velocity of ultrasonic pulses in water are presented for pressures up to about 10,000 kg/cm^2 and for temperatures up to 80°C. Coefficients obtained from least-squares polynomial fittings of the data are also given, together with an analysis of the reliability and reproducibility of the experimental results.

June 23, 1967

Ultrasonic-Velocity Measurements in Water at Pressures to 10,000 kg/cm^2*

1. Introduction. The theory of liquid state is now a lively research field, and the experimental study of the ultrasonic propagation in liquids is one of its most promising tools. During the past decade a large number of investigators have presented evidence of gratifying progress in the technical and theoretical refinement of the study of the velocity and attenuation of liquids; and their data have increasingly helped to test models of the liquid state, for example, those involving molecular relaxation mechanisms. For in the fortunate words of T. A. Litovitz, "The scientist who measures the absorption and velocity of sonic waves and attempts to relate these data to the structure of matter is really an acoustic spectroscopist[1]".

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[1] T. A. Litovitz, J.A.S.A. 30, 383 (1958).

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*This publication is largely based on an invited paper presented before the Acoustical Society on 1 June 1966 (J.A.S.A. 39, 1224, (1966)).

In a few laboratories the experiments have been extended to encompass pressures higher than atmospheric, adding this dimension to the more usual variables such as temperature and frequency; in some cases there is an easily observed change of relaxation frequency with pressure in the tens of megacycles per second per thousand atmospheres of pressure. In other cases, increasing pressure changes the attenuation sufficiently to make it possible to test certain models of the liquid state that were based on data for attenuation at atmospheric pressure.[2] As to velocity

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[2] E.g., by Litovitz and Carnevale [J.A.S.A. 13, 134 (1958)] who have been able to relate the relaxational frequency and the type of liquids.

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measurements at different pressures, they have been used for improving the accuracy of P-V-T data and the derivation of thermodynamic coefficients for determining the nonlinearity coefficient[3] B/A, for dealing with structure problems through observations of dispersion or of changes of the temperature coefficient of sound velocity, etc. In this way, the

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[3] M. P. Hagelberg, G. Holton and S. Kao, J.A.S.A., 41, 564-567 (1967).

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experimental results become of interest for work on the theory of the liquid state. As H. Eyring has said,[4] "There

[4]In T. J. Hughel, edit., Liquids, Structure, Properties, Solid Interactions, Elsevier Publishing Company, 1965, p. 141.

are two quite different approaches to a theory of the liquid state which in fact complement each other. In the deductive approach one proceeds as far as possible strictly mathematically, and when the complications cause this logical procedure to bog down, one resorts to some more or less defensible assumption.... in the other approach one struggles to find a physical model of the liquid state which is as faithful to reality as can be devised and yet be solvable." For both approaches the necessary hard data are often in short supply. This is particularly the case for measurement results at extreme conditions such as those of high pressure, results that any model of the liquid state either must pass as a test, or must build on when the parameters are chosen in the first place.[5]

[5]Davies and Lamb (Proc.Phys.Soc. 73, 767 [1959]), for example, attempt to develop a two-state theory for triethylamine, but having available only data at a single temperature for a pressure run of limited range, they conclude that the lack of data "makes it impossible to test the theory". Repeatedly they stress the need for further experimental work at high pressures, and they end their paper with the remark, "It seems important to us that the questions raised here should be settled, and in particular that further experimental work should be aimed at a systematic study under conditions

of variable pressure and temperature."

Nevertheless, despite the usefulness of velocity and attenuation data in liquids under pressure, only relatively few researchers have systematically exploited this field since 1936 when Bicquard measured attenuation in toluene very roughly to 1,000 atmospheres. In the whole world literature, only about two dozen authors have published results on the velocity of ultrasonic waves at high pressure in any liquid, and fewer still on attenuation. Moreover, the pressures used so far, with very few exceptions, have been in the range to 2,000 atmospheres or less, where the experimental difficulties inherent in high-pressure work tend to become excessively noticeable, owing to the fact that, for example, the available sample space becomes quite small in high-pressure vessels.

2. Apparatus. Our method for ultrasonic velocity measurement is an extension of the pulse-echo method originally adapted by the author in P.W. Bridgman's laboratory for measurements on liquids to about 6,000 kg/cm^2.[6] This paper summarizes more recently developed methods and new data, largely made possible by equipment that has become available since that period.

[6] G. Holton, "Ultrasonic Propagation in Liquids under High Pressures", Technical Memorandum No. 3, ONR Report NR-014-903, Acoustics Research Laboratory, Harvard University, (1948); also J.Appl.Phys. 22, 1407 (1951).

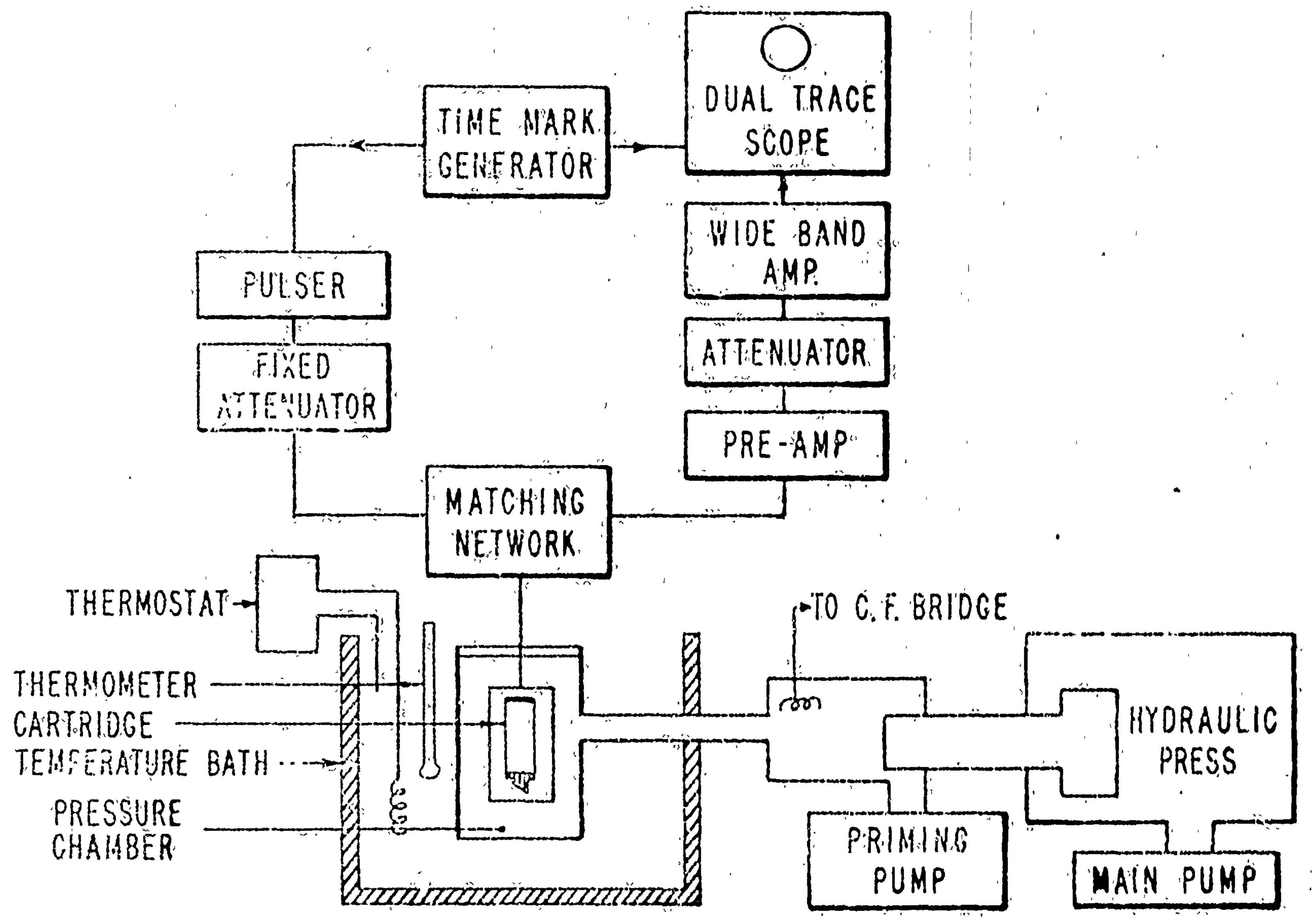
A block diagram of the apparatus is shown in Fig. 1. The pulsed oscillator (Arenberg Laboratories Type PG-650-C) and the sweep delay generator of the oscilloscope (Tektronix 565A) are simultaneously triggered by a pulse from the time-mark generator (Tektronix Type 181). The oscilloscope has a dual channel plug-in unit operated on the alternate mode. The echoes produced by each pulse on being reflected back and forth in chamber containing the liquid sample under test are displayed on one channel, a timing comb from the time-mark generator on the other. The two channels are synchronized and hence the interval between echoes can be interpolated between time marks to a precision of 0.1μ sec. The wideband amplifier and attenuator are also the Arenberg Laboratories units (WA-600-E and Arenberg Laboratories Attenuator).

The pressure system consists of the steel container with an internal chamber about 8 inches long by 0.5 inch diameter. It is within this small space that the experimental sample, transducer, mirror, containing cartridge, sylphone, etc. must be located. A schematic diagram of one of the various cartridges in use is shown in Fig. 2.

The pressure is generated in a two-stage system, a priming pump for the first 2500 kg/cm^2, and a hydraulic ram to about 10,000 kg/cm^2. The pressure in the chamber is measured with a manganin gauge which is in one arm of a Carey-Foster bridge. The gauge is calibrated against the known freezing pressure of mercury at 0°C, namely 7718.5 kg/cm^2.[7]

{caption}

Figure 1. Schematic Diagram of Components for Measuring Sound Velocity and Absorption.



SCHEMATIC DIAGRAM OF COMPONENTS FOR MEASURING SOUND

(caption) Figure 2. Cartridge Assembly.

A sylphone bellows fits on top and transmits the ambient pressure to the liquid sample in the cartridge.

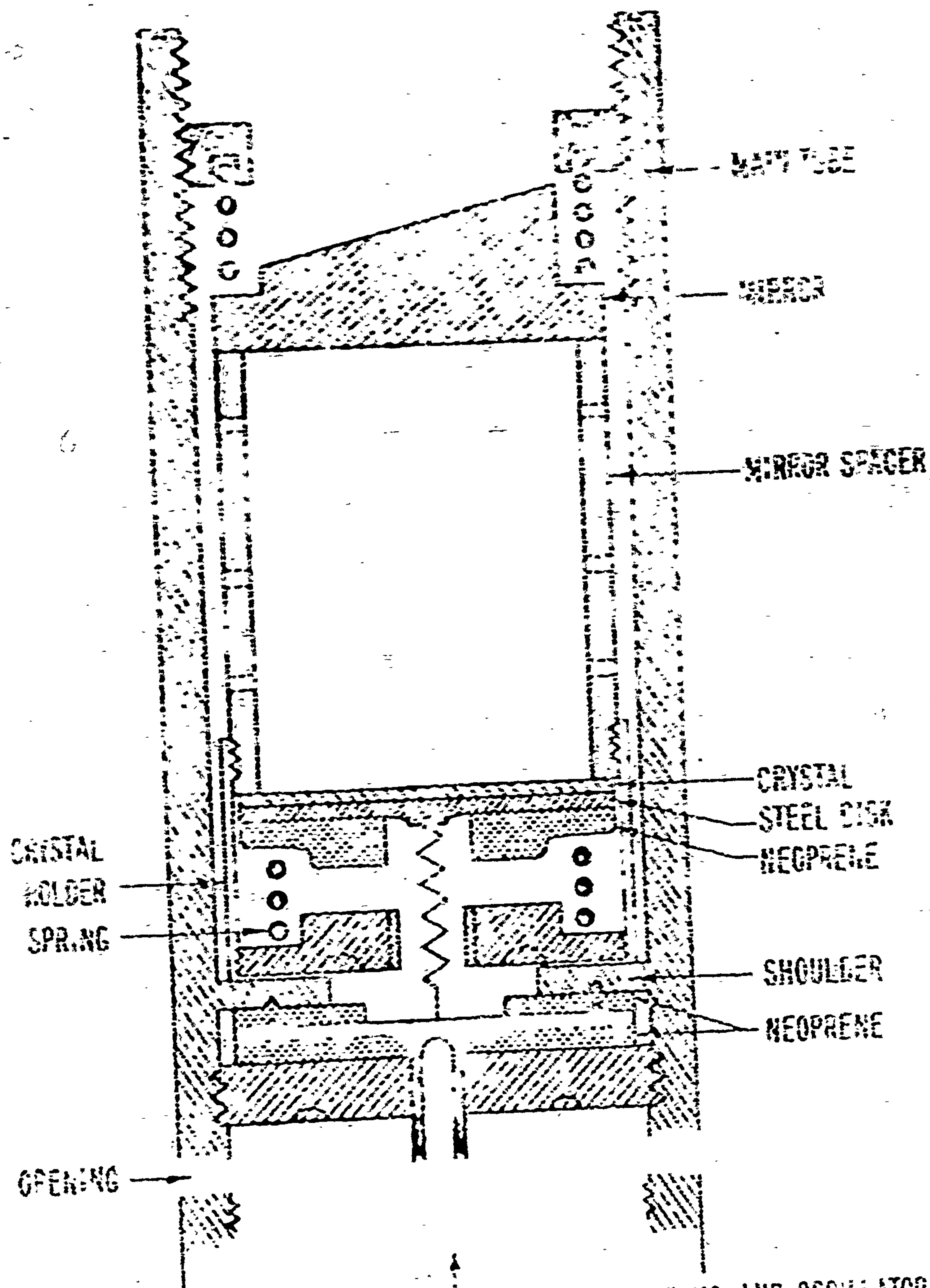

MAIN TUBE
MIRROR
MIRROR SPACER
CRYSTAL
STEEL DISK
NEOPRENE
CRYSTAL
HOLDER
SPRING
SHOULDER
NEOPRENE
OPENING
TO PRESSURE PLUG AND OSCILLATOR

Figure 2

[7] R. S. Dadson and R. G. P. Greig, British J. Appl. Physics 16, 1711 (1965).

The precision of a pressure measurement is ± 3 kg/cm^2.

The velocity measurements are typically made at a frequency of about 15 MHz using an X-cut quartz crystal driven at its fundamental frequency. In the cartridge design shown in Fig. 2, the crystal is held against the stainless steel spacer by a strong spring; the latter fits against the neoprene backing of the stainless-steel electrode in back of the crystal.

A number of stainless steel spacers can be interposed between crystal and mirror, ranging in length to 4.2 cm. This length is limited by the space available in the pressure chamber. The ends of the spacers are ground flat and parallel to within 0.0001 in. The stainless steel mirror is held against the end opposite the transducer by a strong spring and retaining ring. The back of the mirror is beveled to reduce interference by sound reflected from the back of the mirror. The cartridge is closed off from the pressure transmitting liquid at the shoulder in the cartridge by a bellows at the mirror end. This bellows transmits the pressure from the pressure chamber to the test liquid.

The clamping of the crystal is critical; the stiffness of the spring and the thickness of the neoprene backing markedly affect the echo pattern. Since neoprene is attacked

by many of the liquids that have been investigated with this equipment, an alternative backing consisting of a few layers of 0.010 inch teflon discs has been used in those cases.

3. <u>Measurement Procedure</u>. In a typical run, the cartridge is filled with double distilled water at room temperature and atmospheric pressure. The liquid need not be degassed since all available work indicates any effect of dissolved gas on the sound velocity to be much below the accuracy of our measurements. The cartridge is then placed in the pressure chamber, and is allowed to remain at a pressure of about 2000 kg/cm^2 for some time to season the assembly, i.e. to make it more likely that any minor repositioning of components occur before the run is begun rather than during a data-taking run.

In taking the data, the time-mark generator is used to calibrate the oscilloscope directly. Since triggering is accomplished by a pulse from the same time-mark generator which is displayed in one channel of the CRO, both the sweep delay and the sweep itself may be calibrated. The initial rise of the first echo is positioned between two time marks 10μsec apart, and the time of its initial rise may be determined to within 0.1 μsec. This process is repeated until, say, ten echo intervals have been determined. The total time for ten echoes being typically 300-500μsec for the range of temperatures and pressures used and with the

longest spacer, and since the least count is 0.1 μsec, the precision of the timing procedure is better than 0.05 per cent. The time readings are reproducible to the least count, i.e. 0.1 μsec.

The sound velocity is calculated from the average time per echo and the known spacer length, corrected for the pressure and temperature of the experiments. The precision of the calculated sound velocities is then approximately 0.04 per cent. The accuracy of the velocity determinations is not quite that good; the agreement between velocity values so obtained at 1 atm with corresponding published absolute values obtained by very elaborate methods (e.g. at the National Bureau of Standards and the Naval Ordnance Laboratory) is found to be approximately 0.1 per cent. Also, our own results are reproducible to within 0.1 per cent. Therefore the relative accuracy of the measured sound velocity is conservatively taken to be 0.2 per cent in this report. Consequently, some of the numerous sources of error in this kind of work have been neglected, since they appear to be at least an order of magnitude smaller.

4. Velocity Data for Water. Our data on the velocity of ultrasonic pulses in the 15 MHz range in distilled water, to the accuracy cited above, are presented in Tables I and II and in Figures 3 and 4. Table I details values for two typical runs at the same temperature. These runs were not made consecutively, but were separated by more than a year; the agreement is gratifying.

Table I.

Velocity Data for Water at 50°C

Run A		Run B	
$P(kg/cm^2)$	Velocity (m/s)	$P(kg/cm^2)$	Velocity (m/s)
1	1541.9	1	1542.8
313	1595.1	260	1587.2
548	1633.5	525	1631.8
823	1679.5	753	1668.5
1058	1715.5	1046	1715.4
1247	1746.5	1511	1787.2
1502	1784.0	2135	1879.6
1995	1857.2	2164	1882.5
2079	1869.2	2642	1948.2
2938	1988.4	3010	1997.4
2562	1936.6	4036	2125.6
4139	2138.6	4051	2130.9
4949	2232.4	4978	2235.7
6089	2354.8	5996	2344.9
7002	2447.3	7004	2445.5
8057	2544.3	8033	2545.1
		9006	2628.0
		10019	2712.9

Table II

Velocity Data in Terms of Coefficients for Eq.(1)

(Highest pressures to be used:
10^4 kg/cm^2 for 50°,60°,70°C;
8×10^3 kg/cm^2 for 30°,40°C;
6×10^3 kg/cm^2 for 0°C)

T(°C)	No. of data points	average absolute % deviation	r.m.s. deviation (m/s)	max. % deviation	B(1)	B(2)	B(3)	B(4)
0	22	0.09	1.74	0.22	0.15900	1.7439×10^{-5}	-5.9140×10^{-9}	4.5909×10^{-13}
30	14	0.06	1.36	0.16	0.16828	-4.1095×10^{-6}	-3.6601×10^{-10}	3.1075×10^{-14}
40	12	0.03	0.66	0.07	0.16789	-4.3894×10^{-6}	-4.4187×10^{-10}	4.2646×10^{-14}
40	16	0.04	0.80	0.08	0.17007	-6.4579×10^{-6}	6.7279×10^{-11}	5.7377×10^{-15}
50	16	0.03	0.69	0.07	0.17183	-7.5956×10^{-6}	2.1460×10^{-10}	-3.9693×10^{-16}
50	28	0.03	0.96	0.11	0.17424	-8.7474×10^{-6}	3.9024×10^{-10}	8.9305×10^{-15}
60	16	0.03	0.78	0.08	0.17710	-1.0056×10^{-5}	5.0728×10^{-10}	-1.7453×10^{-14}
60	16	0.03	0.63	0.06	0.17802	-1.0396×10^{-5}	5.8115×10^{-10}	-1.6086×10^{-14}
80	13	0.02	0.56	0.09	0.18752	-1.3887×10^{-5}	1.0472×10^{-9}	-3.7574×10^{-14}
80	16	0.04	0.92	0.10	0.18868	-1.4024×10^{-5}	1.0140×10^{-9}	-3.3970×10^{-14}

(caption) Figure 3.

Graph of results for velocities at six temperatures.

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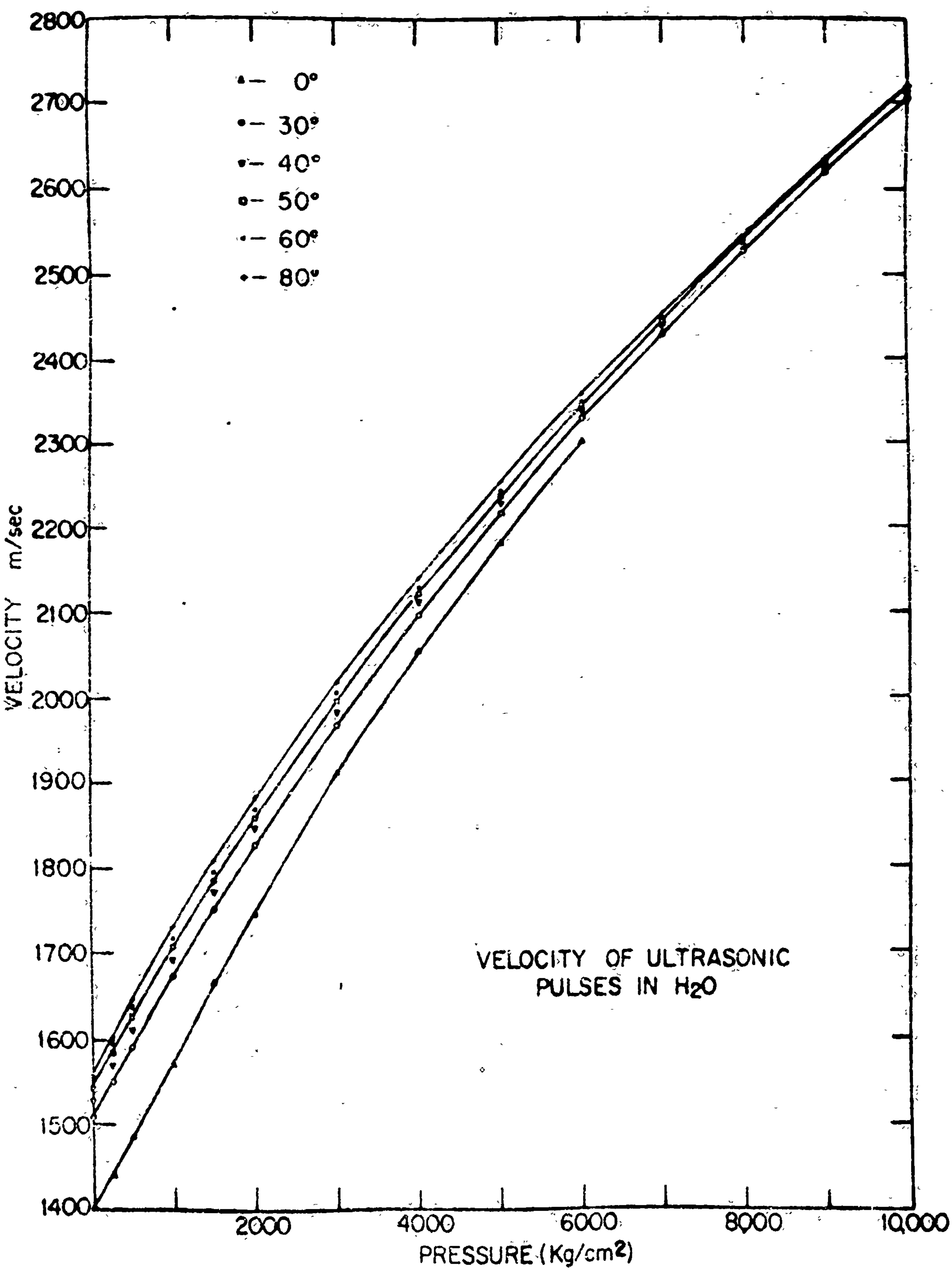
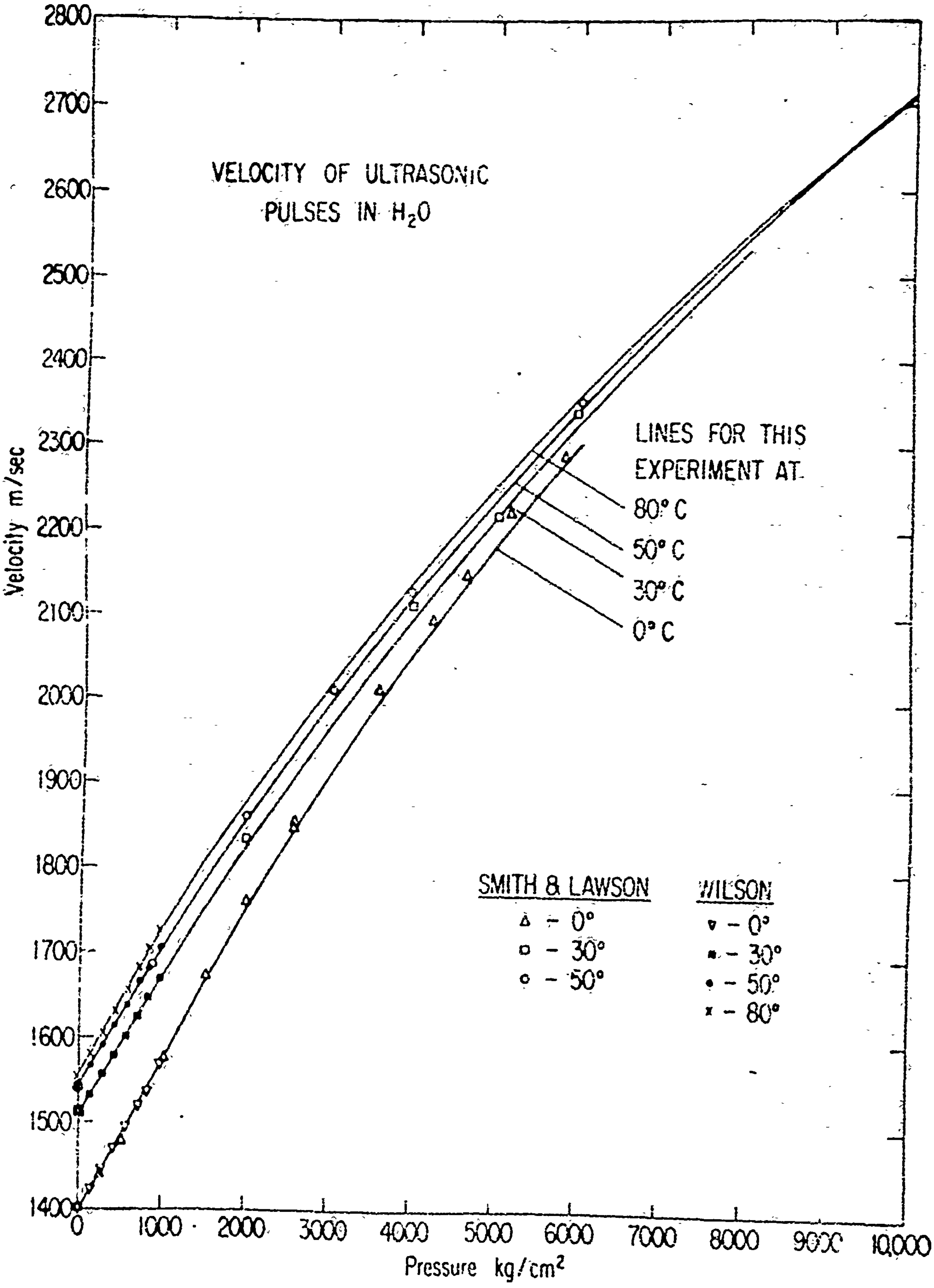


0°
30°
40°
50°
60°
80°
VELOCITY m/sec
2800
2700
2600
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
2000
4000
6000
8000
10,000
PRESSURE (Kg/cm2)
VELOCITY OF ULTRASONIC
PULSES IN H2O

Editor: Always print the captions.

Figure 4. Comparison with two other published sets of data: A. H. Smith and A.W. Lawson, and W. Wilson.



VELOCITY OF ULTRASONIC PULSES IN H_2O
Velocity m/sec
Pressure kg/cm²
2800
2700
2600
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10,000
LINES FOR THIS EXPERIMENT AT
80° C
50° C
30° C
0° C
SMITH & LAWSON
Δ - 0°
□ - 30°
○ - 50°
WILSON
▽ - 0°
■ - 30°
● - 50°
× - 80°

In order to present the data for all temperatures and pressures in a more concise form, we used the IBM 7094 to fit all data for constant temperatures to a fourth degree polynomial in pressure, and determined the coefficients using a least squares program. No weight factors are used in the least squares fit; therefore if the quantity being fitted (velocity) varies greatly over the measured pressure range, the fit will implicitly weight the high end more heavily. Evidently in varying the parameters to determine a minimum for the sum of squares of deviations of calculated from observed values, the program can allow a larger percentage deviation at the low end than at the high end in producing a given variation in the sum of squares. To avoid getting such a weighting toward the high end, we have required the velocity at atmospheric pressure and at each temperature to be held constant to a previously measured, well-known published absolute value. For water we chose M. Greenspan's and C.E.Tschiegg's[8] values;

[8] M.Greenspan and C.E.Tschiegg, J.A.S.A., 31, 75-76(1959). To the level of accuracy in our experiment, we could equally well have used the data of W. D. Wilson [J.A.S.A. 31,1070,(1959)].

they give the velocity (in m/sec) at 1 atm in terms of the temperature T (in °C) as follows:

$$C_G = 1402.736 + 5.03358\,T - 0.0579506\,T^2 + [3.31636 \times 10^{-4}]T^3 - [1.45262 \times 10^{-6}]T^4 + [3.0449 \times 10^{-9}]T^5$$

Our functional form for velocity v which was used in the fit is:

$$v = C_G + B(1)P + B(2)P^2 + B(3)P^3 + B(4)P^4 \quad \text{(Eq. 1)}$$

To keep within the 0.2% limit of accuracy, Eq. (1) must of course not be used beyond pressures for which reliable measurements were available for the computation of the coefficients in Table II. Hence the highest pressures to be used in Eq. (1) are 10,000 kg/cm^2 for 50, 60, and 70°C, 8000 kg/cm^2 for 30 and 40°C, and 6000 kg/cm^2 for 0°C. (The freezing pressure for water is about 6500 kg/cm^2 at 0°C, according to Bridgman.[9])

[9] P. W. Bridgman, Collected Experimental Papers, 1, 559, Harvard University Press (1964).

Table II lists the number of data points used in the fit, the average absolute percent deviation, the root mean square deviation, the maximum percent deviation, and the values of the coefficients in Eq. (1).

5. Tests for Reproducibility. We used the coefficients in Table II to test the reproducibility of our measurements. Since the maximum percent deviation between the polynomial fittings for any two runs can be calculated to be under 0.15 per cent over the usable pressure range, we have combined the two sets of data shown in Table II for 40, 50, 60, and 80°C to produce a single fitted curve for each temperature, and we used the resulting coefficients to calculate round pressure velocities. Table III displays the coefficients and r.m.s. deviations associated with these 4th degree polynomial fits, and Table IV gives the interpolated values for velocities at round pressures. As is suggested, in part, by the lower r.m.s.

Table III

$$v_T(P) = \sum_{j=0}^{4} A_j P^j$$

Constant temperature coefficients for best quartic polynomial fit

in pressure of ultrasonic velocity in water

(Atmospheric value held constant to Greenspan's and Tschiegg's values[8])

Temp.	r.m.s. deviation m/sec.	A0	A1	A2	A3	A4
0°C	1.74	0.140274×10^{4}	.159004	$.174388 \times 10^{-4}$	$-.592402 \times 10^{-8}$	$.459087 \times 10^{-12}$
30°	1.36	0.150944×10^{4}	.168276	$-.410946 \times 10^{-5}$	$-.366008 \times 10^{-9}$	$.310752 \times 10^{-13}$
40°	0.79	0.152918×10^{4}	.169873	$-.622844 \times 10^{-5}$	$.18187 \times 10^{-10}$	$.858353 \times 10^{-14}$
50°	0.97	0.154287×10^{4}	.172941	$-.813470 \times 10^{-5}$	$.298900 \times 10^{-9}$	$-.461496 \times 10^{-14}$
60°	0.88	0.155130×10^{4}	.177420	$-.101182 \times 10^{-4}$	$.552601 \times 10^{-9}$	$-.154456 \times 10^{-13}$
80°	0.36	0.155481×10^{4}	.188188	$-.139947 \times 10^{-4}$	$.103590 \times 10^{-8}$	$-.360131 \times 10^{-13}$

Table XV

Velocity Interpolation at Round Pressures, computed with the coefficients from the best quartic polynomial fit (see Table III).

Pressure (kg/cm^2)	0.0°C	30.0°C	40.0°C	50.0°C	60.0°C	80.0°C
1	1402.7	1509.4	1529.2	1542.9	1551.3	1554.8
500	1485.7	1592.3	1612.4	1627.2	1637.4	1645.3
1000	1573.5	1673.1	1692.7	1707.8	1719.0	1729.8
1500	1663.6	1751.3	1769.9	1784.8	1796.3	1808.8
2000	1750.2	1826.9	1844.2	1858.4	1869.7	1882.8
2500	1834.4	1899.8	1915.4	1928.8	1939.5	1952.4
3000	1913.7	1969.7	1983.8	1996.1	2006.0	2018.3
3500	1987.6	2036.9	2049.4	2060.5	2069.6	2080.9
4000	2056.0	2101.2	2112.3	2122.3	2130.4	2140.6
4500	2119.7	2162.7	2172.6	2181.6	2188.7	2197.8
5000	2180.0	2221.6	2230.4	2238.6	2244.8	2252.7
5500	2239.1	2278.0	2285.9	2293.4	2298.7	2305.8
6000	2299.9	2332.2	2339.2	2346.2	2350.8	2357.1
6500		2384.4	2390.4	2397.1	2401.1	2406.8
7000		2434.9	2439.9	2446.2	2449.8	2455.1
7500		2484.1	2487.6	2493.8	2497.0	2502.0
8000		2532.4	2533.9	2539.9	2542.7	2547.4
8500				2584.6	2587.0	2591.4
9000				2628.0	2629.9	2633.7
9500				2670.3	2671.5	2674.3
10000				2711.5	2711.7	2712.9

deviations obtained for temperatures above 30°C in Tables II and III, we feel that the high temperature data are somewhat more reliable.

Finally, for the purpose of convenience when highest accuracy is not needed, we used all of the data in Table II to obtain a 6th-degree-in-pressure and 4th-degree-in-temperature polynomial fit. The coefficients and r.m.s. deviation are given in Table V. The r.m.s. deviation for this overall fit is, of course, higher than any of the constant temperature fits given above. Nevertheless this set of pressure-temperature coefficients will produce velocities which have a maximum deviation from our actual measurements of less than 0.50%.

6. Comparison with other data. Among others, W. Wilson[9] has made careful

[9] J.A.S.A. 31, 1070 (1959). That work bore out the data published by T.Litovitz and E.Carnevale, J.Appl.Phys., 26 816 (1955).

measurements on distilled water in the pressure range from one to 1000 atm. A comparison between our data and Wilson's in his pressure range shows agreement to within 0.2%. The curves in Fig. 4 indicate the consistency of his measurements with ours, the data points reported by Wilson being plotted against the background of our own data as represented by solid curves taken from Fig. 3. Some time ago, A. Smith and A. W. Lawson[10] reported careful measurements to 0.2% of ultrasonic

[10] J.Chem.Phys. 22, 351 (1954).

velocity in water at pressures up to 9410 kg/cm^2 for some

Table [illegible]

Coefficients for polynomial fitting of velocity

$$V(P,T) = \sum_{i=1}^{5} \sum_{j=1}^{7} B_{ij} T^{i-1} P^{j-1}$$

j \ i	1	2	3	4	
1	1403.0	0.502480x10	-0.569210×10^{-1}	0.288720×10^{-3}	-0.824890×10^{-6}
2	0.170527	-0.328857×10^{-3}	0.747396×10^{-5}	-0.412336×10^{-8}	-0.947432×10^{-12}
3	0.374440×10^{-5}	-0.296347×10^{-6}	0.224777×10^{-8}	-0.184014×10^{-10}	-0.435901×10^{-15}
4	-0.162358×10^{-8}	0.502520×10^{-10}	-0.394573×10^{-12}	0.258504×10^{-14}	0.206796×10^{-19}
5	0.713[illegible]60$\times10^{-13}$	-0.143279×10^{-14}	-0.542344×10^{-20}	0.239159×10^{-21}	0.321438×10^{-23}
6	-0.233887×10^{-20}	-0.856236×10^{-22}	-0.411728×10^{-24}	0.445004×10^{-25}	-0.166768×10^{-27}
7	-0.323227×10^{-24}	-0.167803×10^{-25}	0.217033×10^{-27}	0.140489×10^{-29}	0.250665×10^{-31}

R.m.s. deviation = 1.93 m/s   Max. % deviation = 0.43% [at 0°C]. Maximum pressure for each temperature as shown in Table IV.

temperatures. For those three temperatures where a comparison is directly possible, Figure 4 presents their published data against the background of curves obtained in our recent work.

The apparent systematic and increasing difference seen between our curves and Smith and Lawson's earlier data disappears at once when their data are recalculated to the corrected pressure scale--i.e., fixing the calibration point for 0°C mercury at 7718.5 kg/cm^2, rather than at 7640 kg/cm^2 as did almost everyone until recently. The difference of about 1% in the pressure scales is enough to explain the apparent discrepancy for virtually every point within the combined ranges of precision claimed in both experiments. Table VI shows a more detailed comparison. The velocity corrections at each point for Smith and Lawson's data was made by first calculating the pressure calibration correction and then using the computed values of $\partial v/\partial P$ (which are essentially independent of temperature in this small range).

It should be noted that our curves in Fig. 4 run more or less parallel, but if extrapolated to the region beyond our experiment (and indeed beyond the freezing pressure) would tend to join or cross beyond 10,000 kg/cm^2: at that pressure, the difference of velocities at 50°C and at 80°C is only a few meters. This finding is in accord with Smith and Lawson's and so gives this part of our experiment some added significance. Under the conditions of a high-pressure run a small systematic change in the zero-pressure resistance of the manganin-wire

Editor: Present as one horizontal table, second half to follow after first. G.H.

Table VI

Comparison of data

T = 30°C

$P(kg/cm^2)$	$\partial v/\partial P$	Smith and Lawson Velocity (uncorrected)	Smith and Lawson Velocity (corrected)	Author Velocity (m/s)
1	0.17	1510	1510	1509.4
500	0.17	1593	1592.1	1592.3
1000	0.16	1676	1674.4	1673.1
2000	0.15	1833	1829.9	1826.9
3000	0.14	1981	1976.7	1969.7
4000	0.13	2113	2107.6	2101.2
5000	0.12	2234	2227.8	2221.6
6000	0.11	2341	2334.2	2332.2

T = 50°C

$P(kg/cm^2)$	$\partial v/\partial P$	Smith and Lawson Velocity (uncorrected)	Smith and Lawson Velocity (corrected)	Author Velocity (m/s)
1	0.17	1543	1543	1542.9
500	0.17	1623	1622.1	1627.2
1000	0.16	1704	1702.4	1707.8
2000	0.15	1858	1854.9	1858.4
3000	0.14	2004	1999.7	1996.1
4000	0.13	2135	2129.6	2122.3
5000	0.12	2252	2245.8	2238.6
6000	0.11	2356	2349.2	2346.2

pressure gauge at one temperature would quite easily cause the curves to appear to cross earlier.[11] But the temperature

[11] Smith and Lawson's work had the specific aim of repeating and extending our own early velocity measurements (Ref. 6) with more refined techniques. They found the numerical discrepancies to be within the claimed precision for both experiments in the range below 3,000 atm; above that, the differences were larger, but still, as Smith and Lawson put it, "miniscule from an experimental point of view," (Ref. 10, p.358), so small that "any slight systematic error could easily account for the difference. *A priori*, it would be difficult to say . . . if the difference did not arise from comparable errors in both experiments" (Ref. 10, p.355).

However it is of course not possible to use the presumed first crossing of the velocity curves itself to predict "the behavior of the maximum in the velocity of sound as a function of temperature as the pressure is increased", least of all that this temperature decreases with increasing pressure (Ref. 10, p. 351). Neither this nor any previous author had in fact concluded anything about the temperatures of the velocity *maximum* at high pressures. Indeed, the velocity vs. temperature curves at the higher pressures are so flat that the actual values of temperatures at which the sound velocity is a maximum for any given pressure beyond about 4000 kg/cm^2 have still to be found with certainty.

coefficient of velocity, which for water is abnormal (i.e. positive) would become negative beyond any such a cross-over point. We conclude on the basis of our recent data that by the criterion of the sign of the temperature co-efficient of velocity water remains an abnormal liquid under pressure in the range shown, although the value of $\partial v/\partial T$ tends strongly to zero at the higher pressures.

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13. ABSTRACT

Measurements of the velocity of ultrasonic pulses in water are presented for pressures up to about 10,000 kg/cm^2 and for temperatures up to 80°C. Coefficients obtained from least-squares polynomial fittings of the data are also given, together with an analysis of the reliability and reproducibility of the experimental results.

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